

Garth

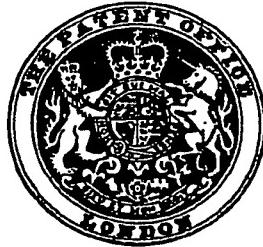
PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Paper-making Compositions and Papers Prepared therewith

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York

5 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to paper-making and more particularly to compositions for the preparation of formaldehyde-free wet-strength papers, and to papers prepared therefrom.

15 Cationic thermosetting polyamide-epichlorohydrin resins have been proposed for imparting wet-strength to paper which are prepared by reacting a polyalkylene-polyamine, preferably containing no more than 8-alkylene groups, with a saturated aliphatic dibasic carboxylic acid containing from 3 to 10 carbon atoms to produce a water-soluble polyamide containing recurring groups of the formula

25 $-\text{NH}(\text{C}_n\text{H}_{2n}\text{HN})_x-\text{CORCO}-$ wherein n and x are integers of 2 or more and R is the divalent hydrocarbon radical of the dibasic carboxylic acid, and then reacting this polyamide with epichlorohydrin. In the above formula, the two nitrogen atoms are attached to different carbon atoms of the $-\text{C}_n\text{H}_{2n}-$ group. The resins are not necessarily prepared from single polyalkylene polyamines, but can be prepared from mixtures of, or crude materials containing, such compounds. A resin prepared as described above is hereinafter termed a "cationic thermosetting polyamide-epichlorohydrin resin of the kind defined".

30 35 40 According to the present invention there is provided an aqueous paper-making composi-

tion comprising cellulose fibre, a cationic thermosetting polyamide-epichlorohydrin resin of the kind defined and a dialdehyde carbohydrate derivative.

45 The invention also provides papers prepared from compositions of the invention.

The paper-making compositions of the invention allow the production of formaldehyde-free papers having excellent wet-strength, comparable with that of paper strengthened by melamine-formaldehyde resin, for example. These papers are particularly useful as supports for those photographic silver halide emulsion layers which are adversely affected by formaldehyde.

50 55 60 In preparing the cationic resin, the mole ratio of polyalkylene-polyamine to dicarboxylic acid should normally be from 0.8:1 to 1.4:1 (preferably from 0.9:1 to 1.2:1), and the quantity of epichlorohydrin per gram-equivalent of the polyamide should normally be from 0.5 mole to 1.8 moles (preferably from 1.0 mole to 1.5 moles).

65 The cationic resin can be dispersed in the slurry at any time prior to that at which the slurry is applied to the wire of the paper machine.

70 75 80 The dialdehyde carbohydrate derivative in a composition of the invention is one of those which can be prepared by treating various materials with periodic acid as described in Specification No. 928,591 and in papers cited therein. Amongst these materials are starch, gum acacia, gum tragacanth, guar gum, mesquite gum, alginic acid, damson gum and hemicellulose gums such as pectins and xylans. Many of these materials are polyuronides and when subjected to controlled periodate oxidation secondary alcohol groups in them are converted to aldehyde groups.

It is preferred for the cationic polyamide-

epichlorohydrin resin to be added to the suspension of cellulose fibre from which the paper is to be prepared prior to the addition of the dialdehyde-carbohydrate. The slurry is then applied to the wire of the paper machine and the paper formed is dried in conventional manner.

It is preferred in preparing paper in accordance with the invention to include therein a small percentage of carboxymethyl-cellulose. Other known paper-making chemicals can be incorporated, including "cationic starch", a starch ether (aminoalkylated starch) as described in United States Patent No. 2,935,436,

stearic size, an alum, and aluminium chloride.

It is preferred for the constituents of a paper-making composition of the invention to be present at concentrations within the following ranges, these concentrations being by weight, based on the dry weight of the cellulose fibre: polyamide-epichlorohydrin resin 0.5—2% dialdehyde carbohydrate derivative 0.25—2%. Suitable concentrations for preferred constituents are:

carboxymethyl-cellulose—0.25—1%
cationic starch—0—3%.

The concentrations used in any particular instance are determined to some extent by the weight of the stock being prepared. For example, in preparing a "double weight" stock approximate concentrations of 0.3% cationic starch, 1% of polyamide-epichlorohydrin resin and 0.75% of dialdehyde carbohydrate derivative are satisfactory. If however the paper is to be of "single weight", larger concentrations of the resin and dialdehyde carbohydrate derivative are in many cases needed for obtaining optimum wet strength.

A paper in accordance with this invention is preferably prepared by subjecting paper-making fibres, such as those of wood-pulp of high alpha-cellulose content to a beating operation in water to form a dilute slurry. To this dilute slurry particularly after some beating has taken place to obtain the desired slowness, the paper-making chemicals are added. The pulp is preferably run through a Jordan machine and the chemicals can either be added at this stage or at some point between the Jordan machine and the headbox. Aluminium chloride or aluminium sulphate is normally added to the pulp slurry to adjust the pH, which can be on the alkaline side if desired. An alkaline pH is preferably obtained by adding ammonium hydroxide.

The stearic size referred to hereinabove can be prepared in known manner: for instance, it can be prepared by mixing together sodium hydroxide and commercial stearic acid. Alternatively a synthetic stearic size such as one in the form of an emulsion can be used.

After the paper is formed it can be tubed in any known manner, for example with a gelatin sizing composition. Other finishing

steps such as calendering can be employed for imparting good surface characteristics to the paper.

As stated above, a paper of this invention is particularly suitable as a base to which is applied a photographic emulsion layer, preferably a paper to be so used is first provided with a baryta coating. However, papers of the invention can usefully be employed for many purposes including towelling, bags, tissue, and maps.

The following examples illustrate the invention.

EXAMPLE 1

An aqueous slurry was prepared using 3000 pounds of high alpha-cellulose sulphite wood pulp fibre. Dye was added followed by stearic size. Also added were 50 pounds of aminoalkylated starch and, after this, aluminium chloride sufficient to adjust the pH. To a portion of the slurry were added 1% (based on dry fibre weight) of a cationic thermosetting polyamide - epichlorohydrin resin of the kind defined and 2% of dialdehyde-starch. This portion of slurry was coated out on the wire of a Fourdrinier, and the paper produced was calendered. The calendered paper was found to have a wet tensile strength of 34 pounds per inch (determined in accordance with TAPPI Standard T456m) approximately the same as that of a comparable paper sized with melamine-formaldehyde resin. To another portion of the slurry were added 1% of the cationic resin and 0.75% dialdehyde-starch, in this order, together with 0.5% of carboxymethyl-cellulose. A paper of outstanding wet tensile strength was made from this portion of slurry.

EXAMPLE 2

2500 pounds of refined wood pulp fibre having a high alpha-cellulose content was slurried and 0.5% of carboxymethyl-cellulose, 2% of cationic starch, gelatin, dyes, stearic size and aluminium chloride (the latter to adjust the pH) were added thereto. To a portion of this slurry, after first beating and processing, were added 0.5% of a cationic thermosetting polyamide-epichlorohydrin resin of the kind defined, and then 0.75% of dialdehyde-starch (all percentages in this Example being based on the weight of dry fibre). Paper was then prepared from the portion of slurry by running it out on the wire of the paper machine followed by calendering. A paper was obtained having a wet tensile strength of 37 pounds per inch. This paper was found to be excellent as a photographic support.

WHAT WE CLAIM IS:—

1. An aqueous paper-making composition comprising cellulose fibre, a cationic thermo-

- setting polyamide-epichlorohydrin resin of the kind defined, and a dialdehyde carbohydrate derivative.
- 5 2. A composition according to Claim 1 wherein the dialdehyde carbohydrate derivative is dialdehyde-starch.
3. A composition according to Claim 1 wherein the dialdehyde carbohydrate derivative is dialdehyde-plant gum.
- 10 4. A composition according to any of the preceding claims which contains from 0.5% to 2% by weight of the resin, based on the weight of the cellulose fibre.
- 15 5. A composition according to any of the preceding claims which contains from 0.25% to 2.0% by weight of the dialdehyde carbohydrate derivative, based on the weight of the cellulose fibre.
- 20 6. A composition according to any of the preceding claims which contains carboxymethyl-cellulose.
- 25 7. A composition according to Claim 6 which contains from 0.25% to 1% by weight of the carboxymethyl-cellulose based on the weight of the cellulose fibre.
8. A composition according to any of the preceding claims which contains cationic starch.
9. A composition according to Claim 8 which contains up to 3% by weight of the cationic starch, based on the weight of the cellulose fibre.
- 30 10. A composition according to any of the preceding claims of which the pH value is greater than 7.
- 35 11. A composition according to Claim 1 in accordance with any of those particularly described herein in Examples 1 and 2.
12. A paper made from a composition according to any of the preceding claims.
- 40 13. A photographic support which comprises a paper according to Claim 12 bearing a baryta layer.
- 45 14. A sensitive photographic material which comprises a support according to Claim 13 bearing a layer of a photographic silver halide emulsion.
- 50 15. A method of making paper which comprises preparing a composition according to any of Claims 1 to 10, and forming paper therefrom.

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